

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 November 2001 (29.11.2001)

PCT

(10) International Publication Number
WO 01/90233 A1

- (51) International Patent Classification⁷: **C08K 5/3475**, 5/3492, 5/315, C08L 69/00
- (21) International Application Number: PCT/US01/05114
- (22) International Filing Date: 16 February 2001 (16.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/575,101 19 May 2000 (19.05.2000) US
- (71) Applicant: **THE DOW CHEMICAL COMPANY**
[US/US]; 2030 Dow Center, Midland, MI 48674 (US).
- (72) Inventor: **VAN NUFFEL, Claude, T., E.**; Muizelstraat
16, B-9041 Oostakker (BE).
- (74) Agent: **CHRISTY, M., Robert**; The Dow Chemical Company,
Intellectual Property, P.O. Box 1967, Midland, MI
48641-1967 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 01/90233 A1

(54) Title: CARBONATE POLYMER COMPOSITIONS COMPRISING LOW VOLATILE UV ABSORBERS

(57) Abstract: Improved carbonate polymer compositions are prepared comprising specific amounts of one or more UV absorbing compounds selected from two or more of the following groups: a hydroxybenzotriazole derivative, a hydroxyphenyltriazine derivative, or a cyanoacrylic acid ester compound wherein all UV absorbing compounds have a molecular weight of at least 400 g/mol. The carbonate polymer compositions according to the invention can be used to prepare molded, shaped or otherwise fabricated articles having improved combinations of protection against UV radiation, color and color stability with reduced plate-out behavior during processing. The compositions are especially suitable for use in extrusion, blow molding, thermoforming, and injection molding.

CARBONATE POLYMER COMPOSITIONS COMPRISING LOW VOLATILE UV ABSORBERS

This invention relates to a carbonate polymer composition which contains low
5 volatile UV absorbers.

Polycarbonate resins offer an excellent balance of properties with respect to
transparency, toughness, dimensional stability and heat resistance. These properties make
polycarbonate an ideal choice for the preparation of many types of molded, shaped or
otherwise fabricated articles, especially including sheets or other structures and parts to be
10 used in glazing and other outdoor applications. However, polycarbonates, like most organic
polymers, degrade when they are exposed to ultraviolet (UV) light. As the polycarbonate
absorbs significant amounts of high energy light and begins to degrade, it is known to
become yellow and hazy and lose its toughness. Since polycarbonates derive much of their
value and utility from their excellent optical properties, that is, low color and high clarity,
15 protection against UV becomes vital.

The use of various types of UV absorbers in the stabilization of polymers is well
known. See for example US-A-3,215,725 (bis cyano-diphenyl-acrylic acid esters);
US-A-4,812,498 (bis benzotriazoles); US-A-5,288,778; GB 2,290,745 and EP 825,226
(triazine compounds); US-A-5,821,380 (multifunctional 2-cyanoacrylic acid esters);
20 EP 68,327 (cyclic imino esters also referred to benzoxazinones) and EP 110,221
(benzophenones and benzotriazoles). These stabilizers function by absorbing incident UV
radiation and dispersing the absorbed energy in a nondestructive manner. Their overall
effectiveness in preventing UV degradation of the polymer depends on numerous factors,
including absorptivity, compatibility, stability and distribution within the polymer. Their
25 UV absorption effectiveness is a function of their concentration in the polymer, especially
near the surface. Concentration of the UV absorber near the surface of the polymer is very
desirable to prevent penetration of UV light and is considered to be more efficient and
economical than dispersion of the UV absorber throughout the bulk of the polymer.

It is critical, therefore, for effective UV stabilization of polymers to have effective
30 concentrations of UV absorbers present near the surface after processing and during long
term. Both chemical and physical losses of the UV absorber will affect the concentration of
UV absorbers in polymers. Chemical losses result from the thermal, photo-oxidative and
oxidative reactions that inactivate or consume the compounds themselves. Physical loss of
the UV absorber involves the removal of material from the surface by evaporation or

dissolution that is not offset by its replacement in the surface layer by diffusion from the bulk polymer

When UV absorbers are physically lost from polymers, this may lead to undesired effects, such as fuming and plate-out in sheet extrusion or juicing and mold sweat during injection molding. All of these phenomena will result in reduced UV absorber concentrations in the resin and reduced production rates due to frequent, necessary cleaning operations of the equipment. Improved retention of an UV absorber conversely provides more effective stabilization in the desired end use as well as better processability in terms of reduced fuming, plate-out, mold sweat, juicing, etc.

Various methods have been used to improve the UV-stability of polycarbonate (PC). Common approaches are to use UV absorbers as additives in the polycarbonate and to apply layers or other surface treatments to prepare structures where the UV absorbers can be concentrated in the surface or outer layers to prevent UV radiation from deeper penetration into and degradation of the main thickness of the PC sheet. A number of methods and techniques have been developed to concentrate UV absorbers near or at the surface of polymeric materials. These include surface impregnation (see for example US-A-3,309,220; US-A-3,043,709; US-A-4,861,664 and US-A-4,937,026); coating a plastic article with solutions containing thermoplastic resins and UV absorbers (see for example US-A-4,668,588 and US-A-4,353,965); thermal bonding of film layers (see for example JP 07-9,560); and coextrusion (see for example EP-A-110,221; EP-A-247,480; EP-A-320,632; EP-A-338,355 and EP-A-825,226; GB 2,290,745 and US-A-4,264,680 and US-A-5,108,835). In these and other coextrusion references, there is an emphasis on the use of higher molecular weight and lower volatility compounds if used in higher concentrations in coextruded surface layers.

However, in the case of polycarbonate formulations and especially co-extrudable compositions, which contain high levels of UV absorbers, it is always desirable to have improved combinations of physical, processing and appearance properties. It is especially desirable to have such improved resins, improved stabilized articles and improved processes where the stabilizers volatilize less and are better maintained in the compositions and articles during and after processing.

It is thus the objective of the present invention to provide improved carbonate polymer compositions and improved molded, shaped or otherwise fabricated articles having appropriate UV protection (for example, appearance stability) especially for outdoor

applications. It is also an objective to provide an improved process for the preparation of these improved molded, shaped or otherwise fabricated articles.

In one embodiment, this invention relates to improved carbonate polymer compositions comprising one or more UV absorbing compounds selected from two or more of the following groups: a hydroxybenzotriazole derivative, a hydroxyphenyl-triazine derivative, or a cyanoacrylic acid ester compound, wherein all UV absorbing compounds have a molecular weight of at least 400 g/mol.

In another embodiment, the present invention is an improved process for preparing a carbonate polymer composition as described hereinabove.

In a further embodiment, the present invention involves a process of extruding or molding (for example, thermoforming, blow molding, injection molding, etc.) an improved carbonate polymer composition prepared as described hereinabove and extruded or molded into an improved extruded or molded article.

In yet a further embodiment, the invention involves extruded or molded articles of an improved carbonate polymer composition as described hereinabove.

It has been found that the improved carbonate polymer compositions and the improved articles which can be prepared have excellent resistance against UV radiation and provide improved combinations of base color and color stability. It has also been found that the UV absorbers added according to the present invention provide reduced levels of color or yellowing in the final carbonate polymer compositions/articles. This can be particularly noticeable in the resin granules when high levels of UV absorbers are incorporated in a resin to be used as the coextrudable surface layer or when there are multiple thickness of extruded sheet or other article that is stacked or lined up together.

It has also been found that the invention provides improved processes for preparing such articles with reduced levels of plate-out, fuming, mold sweat and/or juicing.

All types of carbonate polymers are generally suitable for use in the compositions, articles and processes of the present invention. Many types of suitable carbonate polymers are well known and commercially available. Suitable types of carbonate polymers include linear and branched carbonate polymers as well as blends thereof. As mentioned above, the present invention is directed both to formulations based on carbonate polymers which can be directly used to prepare molded, shaped or otherwise fabricated articles ("bulk stabilized resins") and to formulations based on carbonate polymers which can be used as a surface or

external coating or layer ("capstock resins") to protect substrate articles or core layers which can be a carbonate polymer of the same or different type or some other polymer resin.

The carbonate polymers of the present invention can be prepared using any of the known polycarbonate polymerization processes, including the interfacial process, solution
5 process or the melt or solid state advancement versions of the transesterification carbonate polymer polymerization process.

In general, these carbonate polymers are prepared from one or more multihydric components by reacting the multihydric compound, such as a diphenol, with a carbonate precursor such as phosgene, a haloformate or a carbonate ester such as diphenyl or dimethyl
10 carbonate. Aromatic carbonate polymers are preferred and aromatic diphenols are preferred for use as at least part of the multihydric compound with preferred diphenols including but not limited to 2,2-bis (4-hydroxyphenyl)-propane (bisphenol A), phenol, 4,4'-(9-H-fluorene-9-ylidene)bis (bishydroxyphenylfluorene), 4,4'-thiodiphenol (TDP), 1,1-bis (4-hydroxyphenyl)-1-phenyl ethane (bisphenol AP); phenolphthalein; bis (4-hydroxyphenyl)
15 diphenyl methane; tetrabromobisphenol A (TBBA); and tetrachlorobisphenol A (TCBA). These carbonate polymers also include aromatic carbonate polymers prepared from two or more different dihydric phenols or a combination of a dihydric phenol and a glycol or a hydroxy- or acid-terminated polyester or a dicarboxylic acid in the event a carbonate copolymer or heteropolymer is desired.

20 The linear and branched carbonate polymers suitable for use in the present invention also include carbonate polymers prepared from two or more different multihydroxy compounds, preferably dihydroxy compounds, and preferably phenols, or a combination of a multihydroxy compound, such as a diphenol, and a glycol or a hydroxy- or acid-terminated polyester or a dicarboxylic acid in the event a carbonate copolymer or
25 heteropolymer is desired. It is also possible to employ multifunctional carboxylic acids, especially aromatic carboxylic acids, and prepare poly(ester-carbonate) resins such as the known aromatic poly(estercarbonates). The known silicon-containing carbonate monomers can also be used to prepare silicon-containing carbonate polymers that are suitable for use in the present invention.

30 Suitable types and amounts of chain terminators (typically monophenolic compounds) and, in the case of branched polycarbonates, branching agents (typically phenols having three or more hydroxy groups) can be employed to obtain the desired

molecular weight and branching degrees in the higher molecular weight branched component.

Suitable branching agents are generally one or more of the following: phloroglucin; phloroglucid; 2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-3; 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-2; 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)pentene-2; 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)pentane; 1,3,5-tri(4-hydroxyphenyl)benzene; 1,3,5-tri(2-hydroxyphenyl)benzol; 1,1,1-tri(4-hydroxyphenyl)ethane; 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol; tetra(4-hydroxy-phenyl)methane; trisphenol; bis(2,4-dihydroxyphenyl)ketone; 1,4-bis(4,4-dihydroxytriphenylmethyl)benzene; α,α',α'' -tri(4-hydroxyphenyl)-1,3,5-tri-isopropylbenzene; 3,3-bis(4-hydroxyaryl)oxyindole; isatinbisphenol; 5-chloroisatin; 5,7-dichloroisatin; 5-bromoisatin; trimellitic acid; pyromellitic acid; benzophenonetetracarboxylic acid; and including for the appropriate compounds, the acid chlorides or other condensation reactive derivatives thereof. Specifically preferred branching agents include phloroglucin; phloroglucid; 1,1,1-tri(4-hydroxyphenyl)ethane; trimellitic acid; pyromellitic acid; benzophenonetetracarboxylic acid and acid chlorides thereof; 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol and 1,3,5-tri(4-hydroxyphenyl)benzene.

It has been found that levels of branching agent in the branched carbonate polymer components for use in the present invention should be in the range of from 0.005 to 1.0 mole branching agent per mole of dihydroxy compound, preferably from 0.01 to 0.8, and more preferably from 0.1 to 0.6 mole branching agent per mole of dihydroxy compound.

In general, by whatever production technique it is prepared and whichever type or types it is, the carbonate polymer should have a molecular weight that provides the desired balance of processing features (melt flow rate, melt strength, and shear sensitivity) and physical properties (toughness, and surface properties) according to the known trade-offs between these. In general, the polycarbonate resin should have a weight average molecular weight of at least 18,000, preferably at least 20,000 and more preferably at least 21,000 and not greater than 42,000, preferably not greater than 41,000 and more preferably not greater than 40,000.

In general, branched carbonate polymers are commercially available and should have a weight average molecular weight of at least 22,000, preferably at least 25,000 and more preferably at least 27,000. In order to obtain branched polymer with minimized levels of gels and other beneficial effects of the branched component, it has been found that the

weight average molecular weight of a branched polymer should not be higher than 39,000, preferably not higher than 38,000, most preferably not higher than 37,000. In this range it has been found that the branched carbonate polymer should have a melt flow rate (MFR) determined under conditions of 300°C and 1.2 kilograms mass (300°C/1.2 kg) of at least 2
5 grams per 10 minutes (g/10 min.), preferably at least 2.5 g/10 min. and most preferably at least 3.0 g/10 min. It has been found that the branched carbonate polymer should have a melt flow rate preferably no more than 30 g/10 min., preferably no more than 15 g/10 min. and most preferably no more than 12 g/10 min.

In general, it can be indirectly determined whether there is a sufficient degree of
10 branching in the branched carbonate polymer by measuring the change in shear sensitivity due to the incorporation of the branched carbonate polymer in a carbonate polymer blend composition. These measurements of shear sensitivity can be done by standard techniques with dynamic mechanical spectroscopy (DMS) or by capillary rheometry.

Suitable linear carbonate polymers are known in the literature and commercially
15 available. For purposes of obtaining desired toughness and crack resistance, it has been found that the linear carbonate polymer component should have a weight average molecular weight of at least 18,000, preferably at least 20,000, and most preferably at least 21,000. In order to keep the desired level of polymer melt flow and processability it has been found that the linear carbonate polymer component should have a weight average molecular
20 weight of no more than 42,000, preferably no more than 41,000, most preferably no more than 40,000. In this range it has been found that the linear carbonate polymer should have a melt flow rate of at least 2 g/10 min., preferably at least 2.5 g/10 min. and most preferably at least 3.0 g/10 min. It has been found that the linear carbonate polymer should have a melt flow rate of no more than 80 g/10 min., preferably no more than 40 g/10 min. and most
25 preferably no more than 35 g/10 min.

For the present invention, blend compositions consisting of a branched carbonate polymer and a linear carbonate polymer component can be used. It is understood that the carbonate polymers suitable for use according to the present invention may be a single component carbonate polymer directly obtained from a polymerization process. On the
30 other hand, the carbonate polymer can also be based on a combination of two components of the same type of differing molecular weights and melt flow rates that are blended to obtain the desired intermediate melt flow rate product.

Listed hereinbelow are examples of some preferred carbonate polymers.

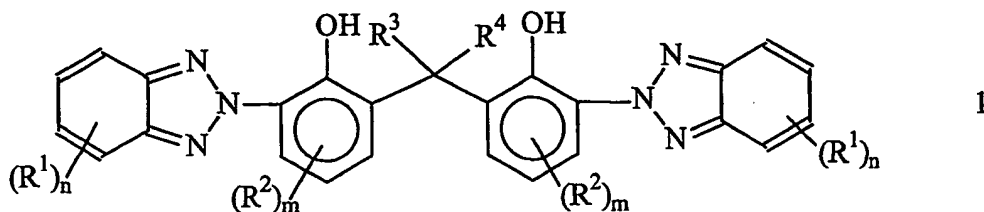
CALIBRE™ brand polycarbonate resins are commercially available from The Dow Chemical Company. The molecular weights of the components are determined by gel permeation chromatography (GPC). The melt flow rate values are measured according to ASTM D-1238 (300°C/1.2 kg) and are reported in g/10 min. Unless otherwise indicated, the references to "molecular weight" herein refer to weight average molecular weights (M_w) determined on the carbonate polymers using gel permeation chromatography with a bisphenol A polycarbonate standard. It should be noted that various references refer to "viscosity average" molecular weight (M_v), which is not the same as "weight average" molecular weight but can be correlated or converted to M_w values. Molecular weight distribution (MWD) is the ratio of weight average molecular weight to number average molecular weight (M_w/M_n).

Preferred Carbonate Polymers

	Carbonate Polymer	MFR	M_w	M_n	MWD	Type
15	CALIBRE 600-3	3	36500	13700	2.66	Branched
	CALIBRE 200-3	3	38700	14200	2.72	Linear
	CALIBRE 200-15	15	26400	10500	2.52	Linear

The carbonate polymer compositions, articles and processes according to the present invention are based on the use of two or more UV absorbers selected from two or more of the following groups: (i) a hydroxybenzotriazole derivative, (ii) a hydroxyphenyltriazine derivative, or (iii) a cyanoacrylic acid ester compound, wherein all UV absorbing compounds of the present invention have a molecular weight equal to or greater than 400 g/mol.

The hydroxybenzotriazole derivatives suitable for use in the present invention are represented by the formula 1:

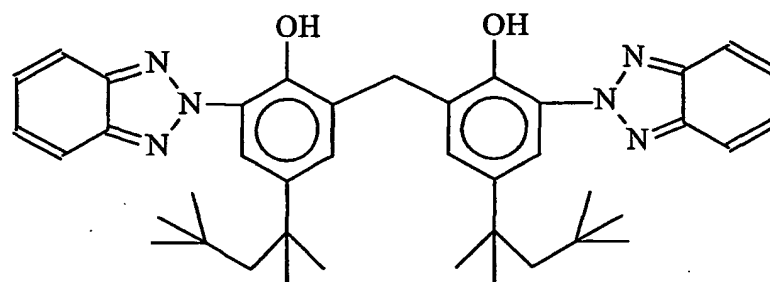


wherein R^1 and R^2 , which may be the same or different, represent H, halogen, C_1 - C_{10} alkyl, C_5 - C_{10} cycloalkyl, C_7 - C_{13} aralkyl, C_6 - C_{14} aryl, OR^5 or $COOR^5$, wherein R^5 represents H or C_1 - C_4 alkyl; R^3 and R^4 may also be the same or different and represent H, C_1 - C_4 alkyl, C_5 or C_6 cycloalkyl, benzyl or C_6 - C_{14} aryl; m represents 1, 2 or 3 and n represents 1, 2, 3, or 4.

5 R^1 preferably represents H, Cl or CH_3 and R^2 preferably represents H, C_1 - C_{10} alkyl, cyclohexyl, C_7 - C_9 aralkyl, phenyl or naphthyl. R^3 and R^4 preferably represent H or C_1 - C_4 alkyl; m preferably represents 1, and n also preferably represents 1.

Particularly preferred hydroxybenzotriazole derivatives (1) are those wherein R^1 represents H; R^2 represents H or C_1 - C_9 alkyl; R^3 represents H; R^4 represents H; m represents
10 1 and n represents 1.

A most preferred example of a hydroxybenzotriazole derivative of this invention is 2,2'-methylene-bis-(6-{2H-benzotriazol-2-yl}-4-{1,1,3,3-tetramethyl-butyl}-phenol) represented by the following structure:

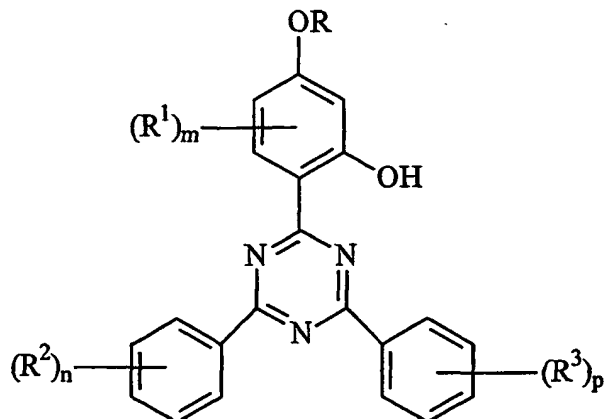


2

15

These higher molecular weight hydroxybenzotriazole derivatives are selected to provide optimized benefits and properties in the areas of UV stabilization performance, improved processability (due to reduced volatility, reduced plate-out, and reduced fuming) and performance and appearance of the final articles. In general, these compounds should
20 have molecular weights equal to or greater than 400, preferably equal to or greater than 500, more preferably equal to or greater than 550 and most preferably equal to or greater than 600 g/mol. In general, at higher molecular weights there is diminishing solubility in polycarbonate and increasing costs and molecular weights of these compounds should not be greater than 2500, preferably not greater than 2000, more preferably not greater than
25 1800, and most preferably not greater than 1600 g/mol.

The hydroxyphenyltriazine derivatives suitable for use in the present invention are taught in US-A-5,288,778 and EP 825. These compounds are generally represented by the following formula:

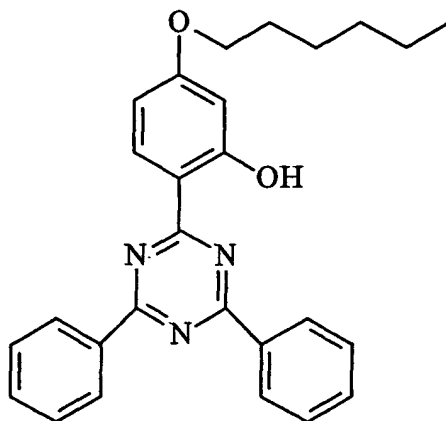


3

- 5 wherein R is hydrogen, C₁ to C₁₈ alkyl, C₂ to C₆ alkyl substituted by halogen or by C₁ to C₁₂ alkoxy, or is benzyl and R¹, R², and R³ which may be the same or different, represent H, halogen, C₁-C₁₀ alkyl, C₅-C₁₀ cycloalkyl, C₇-C₁₃ aralkyl, C₆-C₁₄ aryl, OR⁴ or COOR⁴, wherein R⁴ represents H or C₁-C₄ alkyl; and m represents 1, 2 or 3 and n and p which may be the same or different, represent 1, 2, 3, 4 or 5.

- 10 R¹ preferably represents hydrogen and R² and R³ which may be the same or different, preferably represent H, C₁-C₁₀ alkyl, cyclohexyl, C₇-C₉ aralkyl, phenyl or naphthyl and most preferably H or C₁-C₁₀ alkyl; m preferably represents 1, and n and p which may be the same or different, preferably represent 1 or 2.

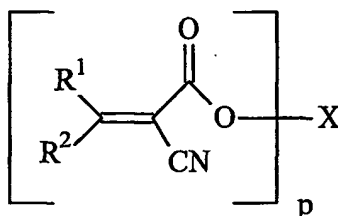
- A most preferred example of a hydroxyphenyltriazine derivative of this invention is
15 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-hexyloxyphenol represented by the following structure:



4

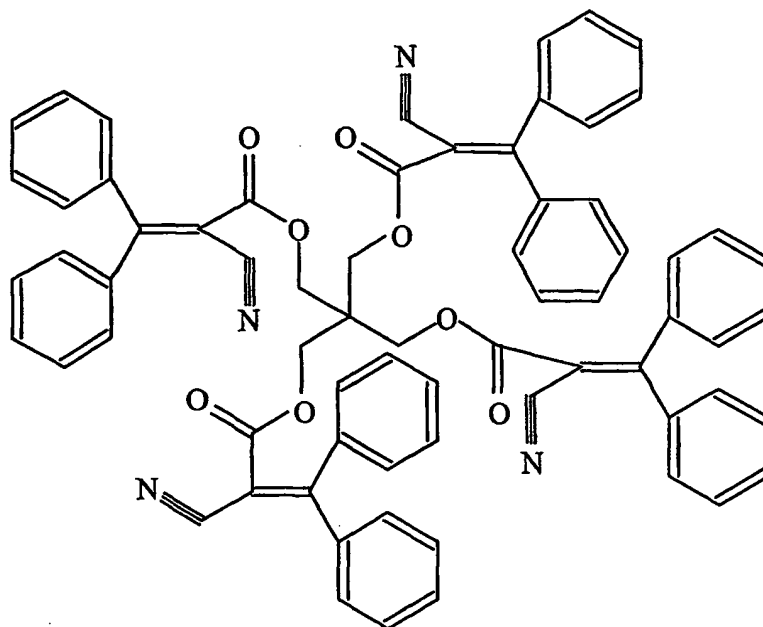
These higher molecular weight hydroxyphenyltriazine derivatives are selected to provide optimized benefits and properties in the areas of UV stabilization performance, improved processability (due to reduced volatility, reduced plate-out, and reduced fuming) and performance and appearance of the final articles. In general, these compounds should have molecular weights equal to or greater than 400 and most preferably equal to or greater than 425 g/mol. In general, at higher molecular weights there is diminishing solubility in polycarbonate and increasing costs and molecular weights of these compounds should not be greater than 2500, preferably not greater than 2000, more preferably not greater than 1800, and most preferably not greater than 1600 g/mol.

The cyanoacrylic acid ester compounds and processes for their preparation suitable for use in the present invention are taught in US-A-5,821,380. These compounds are generally represented by the following formula:



where the R^1 and R^2 substituents are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic nucleus, and at least one of the radicals R^1 or R^2 must be different from hydrogen; p has an average value of from 2 to 10, preferably at least 3 and more preferably has a value of 4; X is the radical of an aliphatic or cycloaliphatic polyol having from 3 to 20 carbon atoms and at least p hydroxyl groups, a cycloaliphatic radical optionally containing 1 or 2 hetero atoms, and an aliphatic radical optionally being interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or C_1 - C_4 -alkylimino groups.

A most preferred example of the UV absorbers of this invention is: 1,3-bis-[(2'-cyano-3',3'-diphenylacryloyl)oxy]-2,2-bis-[(2-cyano-3',3'-diphenylacryloyl)oxy] methyl) propane represented by the following structure:



6

These higher molecular weight cyanoacrylic acid ester compounds are selected to provide optimized benefits and properties in the areas of UV stabilization performance, improved processability (due to reduced volatility, reduced plate-out, and reduced fuming) and performance and appearance of the final articles. In general, these compounds should have molecular weights equal to or greater than 400, preferably equal to or greater than 500, more preferably equal to or greater than 700 and most preferably equal to or greater than 800 g/mol. In general, at higher molecular weights there is diminishing solubility in polycarbonate and increasing costs and molecular weights of these compounds should not be greater than 5000, preferably not greater than 4000, more preferably not greater than 3500, and most preferably not greater than 3000 g/mol.

The amounts of the UV absorbers to be included in the carbonate polymer compositions according to the present invention will vary depending upon whether they are to be employed in "standard" levels throughout the total thickness or bulk of the carbonate polymer to be stabilized or in a concentrate, capstock or surface coating type of resin where relatively high concentrations are employed in order to completely block UV transmittance to the substrate article or layers in a relatively thin layer thickness. In general, to provide UV absorption protection to the carbonate polymers, these compounds can be used in "standard" levels of at least 0.05 weight percent based on weight of carbonate polymer into which the compound is being incorporated, preferably at least 0.10 weight percent, more preferably at least 0.15 weight percent and most preferably at least 0.20 weight percent

based on weight of carbonate polymer. If preparing a concentrate resin, capstock resin or other type of surface coating these compounds can be used in levels of at least 1 weight percent, preferably at least 1.5 weight percent, more preferably at least 2 weight percent, even more preferably at least 2.5 weight percent and most preferably at least 3 weight percent based on weight of carbonate polymer. In general, at higher concentration levels there is diminishing UV protection benefit and levels of these compounds should not be greater than 15 weight percent, preferably not greater than 12 weight percent, more preferably not greater than 10 weight percent and most preferably not greater than 8 weight percent based on weight of carbonate polymer.

The carbonate polymer composition of the present invention may comprise other known stabilizers and amounts commonly used in carbonate polymer compositions of this type, for example antioxidants, light stabilizers, metal deactivators or processing stabilizers which are described, for example, in US-A-5,288,778.

The types and amounts of the stabilizer(s) to be included in the carbonate polymer compositions according to the present invention will vary depending upon the desired balance of combinations of properties and cost. In general, to provide noticeable stabilizing effects and benefits, the stabilizer(s) should be used at levels of at least 5 parts per million (ppm) based on weight of carbonate polymer into which the compound is being incorporated, preferably at least 25 ppm, more preferably at least 50 ppm and most preferably at least 100 ppm. In general, at higher concentration levels there is diminishing benefit and levels of these compounds should not be greater than 5000 ppm, preferably not greater than 3000 ppm, and most preferably not greater than 2000 ppm.

In addition to the UV absorbers and other stabilizers, the carbonate polymer composition according to the present invention can advantageously contain the standard types and amounts of the additive-type components frequently incorporated into carbonate polymers. These components can include ignition resistance additives, fillers (that is, glass fibers, talc, clay, etc.), pigments, dyes, mold release agents, impact modifiers, antistatic additives, and the other additives commonly employed in carbonate polymer compositions.

The resins according to the invention are also advantageously used in blend compositions with other polymer resins such as monovinylidene aromatic polymer optionally containing an impact modifier component (for example, acrylonitrile, butadiene and styrene copolymer (ABS) or acrylonitrile, ethylene-propylene and styrene copolymer (AES)).

Preparation of the carbonate polymer compositions of this invention can be accomplished by any suitable mixing means known in the art, including rollers, kneaders, single screw or multi-screw extruders. The individual components may be dry blended and subsequently melt mixed, either directly in the extruder used to make the finished article
5 (for example, the extruded sheet), or pre-mixing in a separate extruder (for example, a Banbury mixer). Dry blends of the compositions can also be directly injection molded without pre-melt mixing.

Preferably, the carbonate polymer compositions of this invention are thermoplastic. The present invention also involves the use of the carbonate polymer compositions as
10 described above to provide the following wide range of improved processes to prepare molded, shaped or otherwise fabricated articles and improved articles having improved combinations of protection against UV radiation, color and color stability with reduced plate-out behavior during processing. Extrusion, blow molding, thermoforming and injection molding processes for carbonate polymer compositions are well known in the art
15 and commercially practiced for production of a broad range of parts and structures. As is known, extrusion processes for preparing sheet, profiles and like structures involve the steps of melting, forcing the melted polymer through a die, calibration, if needed, and cooling. As is known, blow molding processes for preparing bottles, containers, instrument panels and like structures involve the steps of extrusion or injection molding of an expandable
20 parison, expansion or blowing of the parison to the desired shape and cooling. As is known, thermoforming processes for preparing trays, containers, chocolate molds, and like structures involve the steps of preparing a thermoformable sheet or preform, heating the sheet or preform adjacent to the mold or form of the desired shape, applying a pressure (air pressure or a physical force) or suction to appropriately shape the sheet or preform in the
25 mold or form and cooling. As is known, the injection molding process for lenses, headlamps, lamp covers, and like structures involves the steps of melting, forcing the melted polymer into a mold and cooling.

The improvements in resins, processes and articles and structures according to the present invention are due to the improved UV resistance, improved color and color stability
30 and reduced tendency to plate-out and fuming that provide improved productivity versus a standard resin.

EXAMPLES

The following experiments show the benefits of carbonate polymer compositions according to the present invention in terms of UV stability, prevention of thermal loss of UV absorbers and improved base color and color stability. These Experiments are given to
5 further illustrate the invention and should not be construed as limiting its scope.

Polycarbonate

The polycarbonate resin used in all of the experiments is CALIBRE 200-15 polycarbonate resin. This resin is a linear polycarbonate, has a M_w of 26400 (as measured by GPC) and a melt flow of 15 g/10 min. (as measured by according to ASTM D-1238
10 under conditions of 300°C / 1.2 kg).

UV Absorbers

The following UV absorbers are used in the experiments:

Hydroxybenzotriazole - Tradename LA-31 from Adeka Argus (LA-31)

Molecular weight: 662 g/mol, Chemical name: 2,2'-methylene-bis-(6-{2H-
15 benzotriazol-2-yl}-4-{1,1,3,3-tetramethylbutyl}-phenol);

Hydroxyphenyltriazine – Tradename TINUVIN™ 1577 from Ciba Geigy (1577)

Molecular weight: 429 g/mol, Chemical name: 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-
5-hexyloxyphenol;

Cyanoacrylic acid ester - Tradename UVINUL™ 3030 from BASF (3030)

Molecular weight: 1060 g/mol, Chemical name: 1,3-bis-[(2'-cyano-3',3'-
20 diphenylacryloyl) oxy]-2,2-bis-[(2-cyano-3',3'-diphenylacryloyl) oxy] methyl
propane; and

Benzoxazinone – Tradename CYASORB™ 3638 from Cytec Industries, Molecular weight:
368 g/mol, Chemical name: 2,2'-(1,4-phenylene)bis-[4H-3,1-benzoxazin-4-one].

Determination of Initial Base Color and Color Stability

25

For the purpose of such assessment, the UV absorbers are compounded in the polycarbonate feedstocks at levels between 1500 and 45,500 ppm (0.15 and 4.55 weight percent) on a ZSK-25 twin screw co-rotating Werner and Pfleiderer extruder. The temperature profile used in the extruder is 240°C, 250°C, 260°C, 270°C, 280°C, 290°C,
30 300°C, and 300°C.

Prior to compounding, the polycarbonate is dried at 120°C for 4 hours. The initial base color is measured on the produced granules using a Hunterlab COLORQUEST™ Colorimeter. Granules are placed in a 50mm by 50mm by 50mm quartz cuvette and color is

measured in Reflection mode. Color is expressed using the Yellowness Index (YI) D1925 as well as the CIE Lab L*, a* and b* values. Each measurement is repeated at least five times and an average is calculated.

The polycarbonate granules are subsequently injection molded into color chips on an Arburg 800-325 ALLROUNDER™ 370 CMD injection molding machine. The color is measured on the 3.0 mm plaques using the Hunterlab COLORQUEST Colorimeter. For the transparent polycarbonate, the measurement is done using the Transmission mode. As color data, the YI as well as the CIE Lab L*, a* and b* values are recorded. Each measurement is repeated at least five times and an average is calculated.

Injection molding conditions are varied in order to assess the sensitivity of the various resins on initial color and color stability. Particularly, injection molding temperatures at the die of 320°C and 380°C are used, when UV absorber levels are below 1 weight percent. At higher UV absorber levels, injection molding temperatures at the die of 280°C are used. All other molding parameters are kept constant.

An increasing temperature profile from hopper to die is used. Per zone, an increment of 10°C is set. For instance, for a die set temperature of 380°C, a temperature profile 340°C, 350°C, 360°C, 370°C, and 380°C is used. For the sake of simplicity, only the die set temperature is mentioned in the experiments.

The barrel residence time is kept constant by adjusting the machine cycle time at 40 seconds. Taking into account the barrel volumes and part weight, this corresponds to a total barrel residence time of 5 minutes. A five-step holding pressure profile is used in each case. Per step, holding pressure is decreased by 100 bar. A typical holding pressure profile was 1200-1100-1000-900-800 bar. During molding, part weight is monitored continuously. When a deviation occurs, this is corrected by adjusting holding pressures. Corrective actions are made in steps of 100 bar over the entire holding pressure profile.

The difference between the color measured at die temperatures of 380°C (YI_{380°C}) and at 320°C (YI_{320°C}) is regarded as a measure for the thermal stability of the polycarbonate materials (Δ YI).

UV-Stability Testing

Injection molded plaques, as molded in the thermal stability study (condition 320°C), are evaluated in a QUV-B test using 313 nanometer (nm) lamps and a cycle of 4 hours of UV irradiation at 60°C followed by 4 hours of exposure to water condensation at 50°C (in a heated saturated mixture of air and water vapor - ASTM G 53-88).

The difference between the color for a 320°C molded plaque before (YI_{320°C}) and after 700 hours of QUV-B exposure (UV YI_{320°C}) is regarded as a measure for the UV stability of the polycarbonate materials (UV ΔYI).

Determination of Loss Of UV Additive

5 Loss of UV absorber from a polymer plaque experiments are performed as follows. For the purpose of such assessment, granules of the carbonate polymer compositions containing the UV additives, prepared as discussed above, are taken and compression molded on an Akila compression molding press at a temperature of 260°C into square plaques of 50 mm by 50 mm and having a thickness of 0.5 mm.

10 On these plaques, initial UV absorber contents is determined using a HPLC analysis technique. These plaques are placed in an air-circulated oven at various temperatures for various residence times. After the oven exposure, the contents of the UV absorber are measured again and compared to the initial content.

15 The decrease in UV absorber contents can be regarded as a measure for the degree of fuming and plate-out that can be experienced during material processing such as injection molding or (co)extrusion of sheet structures. Loss of UV absorber is reported as weight percent (wt percent) loss and percentual (%) loss based on the initial weight of the UV absorber in the carbonate polymer composition.

20 Examples 1 to 3 and Comparative Examples A to G are prepared from polycarbonate 200-15 and various UV absorbers using the compounding conditions described hereinabove. Base color (YI), color stability (ΔYI), and UV stability (UV ΔYI) are evaluated according to the techniques described hereinabove. The amount of UV absorbers and performance properties are shown in Table 1, weight percent is based on the weight of the carbonate polymer composition.

25 Examples 4 to 6 and Comparative Examples H to J are prepared from polycarbonate 200-15 and various UV absorbers using the compounding conditions described hereinabove. Base color on pellets (YI) and on plaques molded at 280°C (YI_{280°C}) is evaluated according to the techniques described hereinabove. The amount of UV absorbers and YI and YI_{280°C} performance properties are shown in Table 2, weight percent is based on the weight of the
30 carbonate polymer composition.

Loss of UV absorbers for Examples 4 to 6 and Comparative Examples H to J is determined over a temperature range from 240°C to 280°C over a period of 80 minutes and the results are presented in Tables 3 to 11.

Table 1

5

Example Comparative	1	2	3	A	B	C	D	E	F	G
UV Absorber, wt percent										
LA-31	0.15		0.15	0.15			0.3			
1577	0.15	0.15			0.15			0.3		
3030		0.15	0.15			0.15			0.3	
3638				0.15	0.15	0.15				0.3
Performance										
Granules										
YI	9.54	8.93	6.67	5.77	7.13	5.89	6.11	10.33	6.28	4.27
Plaques										
YI _{320°C}	4.36	3.67	3.74	2.93	2.95	2.91	3.70	4.35	2.89	2.50
YI _{380°C}	4.45	4.48	4.53	4.88	5.18	11.61	4.01	4.79	3.89	4.97
Δ YI	0.09	0.81	0.79	1.95	2.23	8.70	0.31	0.44	1.00	2.47
After 700 hr QUV-B										
UV YI _{320°C}	12.93	12.85	13.39	13.08	14.47	13.36	13.84	13.44	14.02	13.02
UV Δ YI	8.57	9.18	9.65	10.15	11.52	10.45	10.14	9.09	11.13	10.52

Table 2

Example Comparative	4	5	6	H	I	J
UV Absorber, wt %						
LA-31	2.48		2.29	3.94		
1577	2.48	2.40			4.13	
3030		2.37	2.29			4.55
Performance						
Granules						
YI	37.65	36.57	29.90	27.97	40.94	27.54
Plaques						
YI _{280°C}	19.89	18.46	13.94	13.33	23.57	13.60

5

Table 3

Ex. 4: Loss of LA-31	Time, minutes				
Temperature, °C	0	20	40	60	80
240	2.48	2.31	2.28	2.18	2.11
260	2.48	2.24	2.22	1.91	1.69
280	2.48	2.12	1.85	1.83	1.37
Loss, wt percent					
240	0	0.17	0.20	0.30	0.37
260	0	0.24	0.26	0.57	0.79
280	0	0.62	0.96	1.05	1.30
Loss, percent					
240	0	6.9	8.1	12.1	14.9
260	0	9.7	10.5	23.0	31.9
280	0	25.0	38.7	42.3	52.4

Table 4

Ex. 4: Loss of 1577	Time, minutes				
Temperature, °C	0	20	40	60	80
240	2.48	2.40	2.36	2.35	2.28
260	2.48	2.38	2.35	2.24	1.82
280	2.48	2.12	1.85	1.83	1.37
Loss, wt percent					
240	0	0.08	0.12	0.13	0.20
260	0	0.10	0.13	0.24	0.66
280	0	0.36	0.63	0.65	1.11
Loss, percent					
240	0	3.2	4.8	5.2	8.1
260	0	4.0	5.2	9.7	26.6
280	0	14.5	25.4	26.2	44.8

Table 5

Ex. 5: Loss of 1577	Time, minutes				
Temperature, °C	0	20	40	60	80
240	2.40	2.39	2.34	2.32	2.26
260	2.40	2.25	2.22	2.06	2.01
280	2.40	2.16	1.90	1.88	1.67
Loss, wt percent					
240	0	0.01	0.06	0.08	0.14
260	0	0.15	0.18	0.34	0.39
280	0	0.24	0.50	0.52	0.73
Loss, percent					
240	0	0.4	2.5	3.3	5.8
260	0	6.3	7.5	14.2	16.3
280	0	10.0	20.8	21.7	30.4

Table 6

Ex. 5: Loss of 3030	Time, minutes				
Temperature, °C	0	20	40	60	80
240	2.37	2.28	2.23	2.20	2.17
260	2.37	2.27	2.20	2.18	2.14
280	2.37	2.21	2.18	2.14	2.06
Loss, wt percent					
240	0	0.09	0.14	0.17	0.20
260	0	0.10	0.17	0.19	0.23
280	0	0.16	0.19	0.23	0.31
Loss, percent					
240	0	3.8	5.9	7.2	8.4
260	0	4.2	7.2	8.0	9.7
280	0	6.8	8.0	9.7	13.1

Table 7

Ex. 6: Loss of LA-31	Time, minutes				
Temperature, °C	0	20	40	60	80
240	2.29	2.27	2.19	2.16	1.95
260	2.29	2.19	2.14	1.79	1.62
280	2.29	1.69	1.33	1.30	0.97
Loss, wt percent					
240	0	0.02	0.10	0.13	0.34
260	0	0.10	0.15	0.50	0.67
280	0	0.60	0.96	0.99	1.32
Loss, percent					
240	0	0.9	4.4	5.7	14.8
260	0	4.4	6.6	21.8	29.3
280	0	26.2	41.9	43.2	57.6

Table 8

Ex. 6: Loss of 3030	Time, minutes				
Temperature, °C	0	20	40	60	80
240	2.25	2.25	2.19	2.14	2.09
260	2.25	2.23	2.18	2.10	2.04
280	2.25	2.19	2.15	2.10	2.03
Loss, wt percent					
240	0	0	0.06	0.11	0.16
260	0	0.02	0.07	0.15	0.21
280	0	0.06	0.10	0.15	0.22
Loss, percent					
240	0	0	2.7	4.9	7.1
260	0	0.9	3.1	6.7	9.3
280	0	2.7	4.4	6.7	9.8

Table 9

Com. Ex. H: Loss of LA-31	Time, minutes				
Temperature, °C	0	20	40	60	80
240	3.94	3.48	3.18	3.10	2.98
260	3.94	3.10	2.86	2.20	1.86
280	3.94	2.38	1.90	1.35	1.02
Loss, wt percent					
240	0	0.46	0.76	0.84	0.96
260	0	0.84	1.08	1.74	2.08
280	0	1.56	2.04	2.59	2.92
Loss, percent					
240	0	11.7	19.3	21.3	24.4
260	0	21.3	27.4	44.2	52.8
280	0	39.6	51.8	65.7	74.1

Table 10

Com. Ex. I: Loss of 1577	Time, minutes				
Temperature, °C	0	20	40	60	80
240	4.13	3.98	3.73	3.64	3.59
260	4.13	3.53	3.32	3.00	2.76
280	4.13	3.32	2.96	2.54	2.46
Loss, wt percent					
240	0	0.15	0.40	0.49	0.64
260	0	0.60	0.81	1.13	1.38
280	0	0.81	1.17	1.59	1.67
Loss, percent					
240	0	3.6	9.7	11.9	13.1
260	0	14.5	19.6	27.4	33.2
280	0	19.6	28.3	38.5	40.4

Table 11

Com. Ex. J: Loss of 3030	Time, minutes				
Temperature, °C	0	20	40	60	80
240	4.55	4.51	4.46	4.34	4.28
260	4.55	4.33	4.28	4.23	4.09
280	4.55	4.28	4.18	4.04	3.85
Loss, wt percent					
240	0	0.04	0.09	0.21	0.27
260	0	0.22	0.27	0.32	0.46
280	0	0.27	0.37	0.51	0.70
Loss, percent					
240	0	0.9	1.9	4.5	6.0
260	0	4.8	6.0	7.0	10.2
280	0	6.0	8.1	11.3	15.3

5

From these data, it can be concluded that the carbonate polymer compositions of the present invention comprising one or more UV absorbing compounds having a Mw greater than 400 g/mol. selected from two or more of the following groups: a hydroxybenzotriazole derivative, a hydroxyphenyltriazine derivative, or a cyanoacrylic acid ester compound yield the best balance of base color, color stability, UV stability and physical retention of UV absorber when compared with controls using a hydroxybenzotriazole derivative, a

10

hydroxyphenyltriazine derivative, or a cyanoacrylic acid ester compound in combination with a benzoxazinone compound or using a hydroxybenzotriazole derivative, a hydroxyphenyltriazine derivative, a cyanoacrylic acid ester compound or a benzoxazinone compound individually.

- 5 It can be seen that carbonate polymer compositions, articles and fabrication techniques according to the invention provide improved combinations of resistance against UV-radiation, color and color stability, and retention of UV absorber in the resin during processing ensuring negligible levels of fuming, plate-out, mold sweat, juicing, etc. It has been found that the present invention provided improved processes for preparing, among
- 10 other things, extruded sheet structures, blow molded, thermoformed, injection molded, injection blow molded, injection compression molded, film blow molded or foamed parts or structures. It can be seen that the resulting parts or structures according to the present invention are surprisingly improved by use of the described carbonate polymer compositions and the molded, shaped or otherwise fabricated articles will have improved
- 15 combinations of physical and appearance properties including particularly improved UV resistance, color, color stability, cracking resistance and surface properties, without giving problems of thermal loss of the UV absorbers, resulting in problems of plate-out, fuming, mold sweat and juicing, which all reduce the production rate in commercial applications.

CLAIMS

1. A carbonate polymer composition comprising:

(a) a carbonate polymer

and

(b) one or more UV absorbing compounds selected from two or more of the following groups:

(i) a hydroxybenzotriazole derivative,

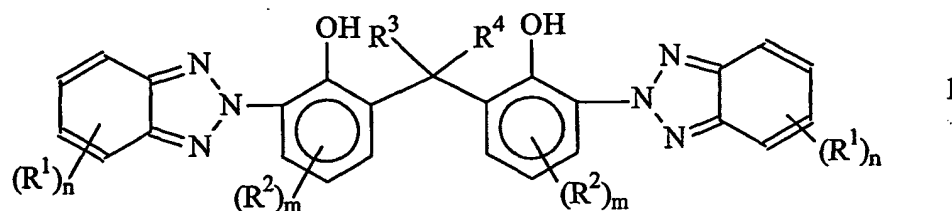
(ii) a hydroxyphenyltriazine derivative or

(iii) a cyanoacrylic acid ester compound

wherein all UV absorbing compounds (i), (ii) and (iii) have a molecular weight of at least 400 g/mol.

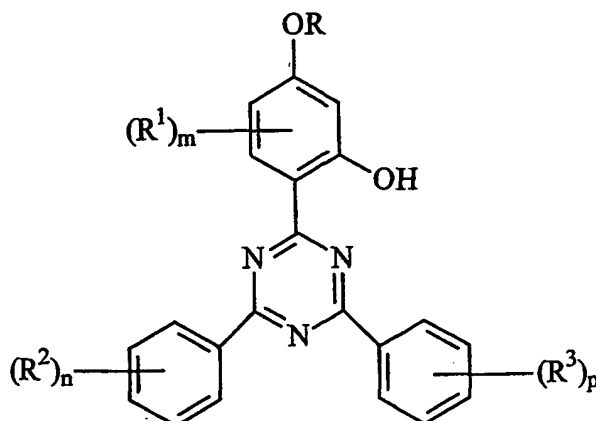
2. A carbonate polymer composition according to Claim 1 wherein the amounts of the UV absorbing compounds which may be the same or different, are from 0.05 to 15 weight percent.

3. The carbonate polymer composition of Claim 1 wherein (b)(i) the hydroxybenzotriazole derivative is represented by formula 1



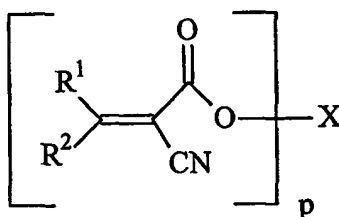
wherein R^1 and R^2 , which may be the same or different, represent H, halogen, C_1 - C_{10} alkyl, C_5 - C_{10} cycloalkyl, C_7 - C_{13} aralkyl, C_6 - C_{14} aryl, OR^5 or $COOR^5$, wherein R^5 represents H or C_1 - C_4 alkyl; R^3 and R^4 may also be the same or different and represent H, C_1 - C_4 alkyl, C_5 or C_6 cycloalkyl, benzyl or C_6 - C_{14} aryl; m represents 1, 2 or 3 and n represents 1, 2, 3, or 4.

4. The carbonate polymer composition of Claim 1 wherein (b)(ii) the hydroxyphenyltriazine derivative is represented by formula 3



5 wherein R is hydrogen, C₁ to C₁₈ alkyl, C₂ to C₆ alkyl substituted by halogen or by C₁ to C₁₂ alkoxy, or is benzyl and R¹, R², and R³ which may be the same or different, represent H, halogen, C₁-C₁₀ alkyl, C₅-C₁₀ cycloalkyl, C₇-C₁₃ aralkyl, C₆-C₁₄ aryl, OR⁴ or COOR⁴, wherein R⁴ represents H or C₁-C₄ alkyl; and m represents 1, 2 or 3 and n and p represent 1, 2, 3, 4 or 5.

10 5. The carbonate polymer composition of Claim 1 wherein (b)(iii) the cyanoacrylic acid ester compound is represented by formula 5



15 where the R₁ and R₂ substituents are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic nucleus, and at least one of the radicals R₁ or R₂ must be different from hydrogen; p has an average value of at least 3; X is the radical of an aliphatic or cycloaliphatic polyol having from 3 to 20 carbon atoms and at least p hydroxyl groups, a cycloaliphatic radical optionally containing 1 or 2 hetero atoms, and an aliphatic radical optionally being interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or C₁-C₄-alkylimino groups.

20 6. A carbonate polymer composition comprising:

(a) a carbonate polymer

and

(b) at least two UV absorbing compounds selected from:

(i) 2,2'-methylene-bis-(6-{2H-benzotriazol-2-yl}-4-{1,1,3,3-tetramethylbutyl}-phenol),

(ii) 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-hexyloxyphenol,

or

(iii) 1,3-bis-[(2'-cyano-3',3'-diphenylacryloyl)oxy]-2,2-bis-[(2-cyano-3',3'-diphenylacryloyl) oxy] methyl) propane.

10 7. A process for preparing a carbonate polymer composition which comprises the step of combining:

(a) a carbonate polymer

and

15 (b) one or more UV absorbing compounds selected from two or more of the following groups:

(i) a hydroxybenzotriazole derivative,

(ii) a hydroxyphenyltriazine derivative, or

(iii) a cyanoacrylic acid ester compound

20 wherein all UV absorbing compounds (i), (ii) and (iii) have a molecular weight of at least 400 g/mol.

8. A process for producing an extruded or molded article of a carbonate polymer composition comprising the steps of:

(A) preparing a carbonate polymer composition which comprises the step of combining:

25 (a) a carbonate polymer

and

(b) one or more UV absorbing compounds selected from two or more of the following groups:

(i) a hydroxybenzotriazole derivative,

30 (ii) a hydroxyphenyltriazine derivative, or

(iii) a cyanoacrylic acid ester compound

wherein all UV absorbing compounds (i), (ii) and (iii) have a molecular weight of at least 400 g/mol,

and

(B) extruding or molding the carbonate polymer composition into an extruded or molded article.

9. The composition of Claim 1 in the form of a molded or extruded article.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/3475 C08K5/3492 C08K5/315 C08L69/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 821 380 A (ANMUELLER ALEXANDER ET AL) 13 October 1998 (1998-10-13) column 5, line 23 - line 25 column 5, line 55 column 6, line 4 - line 12 column 6, line 56 - line 57 column 7, line 1 - line 6 ---	1-9
X	US 5 288 778 A (BURDESKA KURT ET AL) 22 February 1994 (1994-02-22) column 1, line 43 - line 66 column 2, line 37 column 4, line 46 column 5, line 17 - line 30 column 7, line 60 column 8, line 12 column 10, line 4 - line 26; claims --- -/--	1-5, 7-9

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

11 June 2001

Date of mailing of the international search report

19/06/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Droghetti, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 900 823 A (GENERAL ELECTRIC COMPANY) 10 March 1999 (1999-03-10) page 1, line 34 - line 46 page 5, line 19 -page 6, line 29 page 7, line 5 - line 9 -----	1-9

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5821380	A	13-10-1998	DE 4440055 A	15-05-1996
			DE 19519895 A	05-12-1996
			AU 3980395 A	06-06-1996
			BG 101460 A	31-08-1998
			BR 9509644 A	16-09-1997
			CA 2204430 A	23-05-1996
			CN 1162955 A, B	22-10-1997
			CZ 9701349 A	15-04-1998
			WO 9615102 A	23-05-1996
			EP 0790980 A	27-08-1997
			EP 0900782 A	10-03-1999
			FI 971991 A	09-05-1997
			JP 10511081 T	27-10-1998
			NO 972156 A	09-07-1997
			PL 320203 A	15-09-1997
			SK 56097 A	08-07-1998
US 5288778	A	22-02-1994	BR 9200567 A	27-10-1992
			CA 2061486 A	22-08-1992
			DE 59208822 D	02-10-1997
			EP 0500496 A	26-08-1992
			ES 2107518 T	01-12-1997
			HK 1002331 A	14-08-1998
			JP 5093089 A	16-04-1993
			KR 228412 B	01-11-1999
			SG 49848 A	20-07-1999
EP 0900823	A	10-03-1999	US 5869554 A	09-02-1999
			CN 1210120 A	10-03-1999
			JP 11152404 A	08-06-1999
			SG 67540 A	21-09-1999